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6. AUTHORS
Dipankar Roy, Sitaraman Krishnan, John McLaughlin

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Clarkson University
8 Clarkson Avenue
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14. ABSTRACT
Non-volatile, non-flammable and polymerizable ionic liquid (IL) electrolytes for high-performance dye sensitized solar cells (DSSCs) have been synthesized and characterized. These ILs serve as promising electrolytes for advanced dye sensitized solar cells (DSSCs). We have characterized the thermo-physical and electrochemical properties of these ILs for DSSC-specific applications. Computer simulations have been performed to understand the structural properties of the new electrolytes/nano-composite systems

15. SUBJECT TERMS
Subject Terms: Subject Terms (list keywords that describe the report): Dye sensitized solar cell, ionic liquid electrolyte, electrochemical characterization, computer simulation, smart materials, sensors

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Report Title

Report Information for Project 2:

ABSTRACT

Non-volatile, non-flammable and polymerizable ionic liquid (IL) electrolytes for high-performance dye sensitized solar cells (DSSCs) have been synthesized and characterized. These ILs serve as promising electrolytes for advanced dye sensitized solar cells (DSSCs). We have characterized the thermo-physical and electrochemical properties of these ILs for DSSC-specific applications. Computer simulations have been performed to understand the structural properties of the new electrolytes/nano-composite systems

Report Information for Project 2:

Authors: Sitaraman Krishnan, John McLaughlin and Dipankar Roy

Subject Terms: Subject Terms (list keywords that describe the report): Dye sensitized solar cell, ionic liquid electrolyte, electrochemical characterization, computer simulation, smart materials, sensors

Abstract: 200 word limit. Plain text only, do not copy diagrams, formulas, etc. instead use the attachment at the bottom of the menu. But Please do enter the abstract in a plain text form, it is used in an overall summary report within the Army.

Non-volatile, non-flammable and polymerizable ionic liquid (IL) electrolytes for high-performance dye sensitized solar cells (DSSCs) have been synthesized and characterized. These ILs serve as promising electrolytes for advanced dye sensitized solar cells (DSSCs). We have characterized the thermo-physical and electrochemical properties of these ILs for DSSC-specific applications. Computer simulations have been performed to understand the structural properties of the new electrolytes/nano-composite systems

Sub Contractors: None

Inventions: One patent application has been filed.

Title of invention: Solid Organic Electrolytes

Application Number: 12/778,410

Is the Patent Filed in the US? Yes

Is the Patent Filed in a Foreign Country? No

Was the confirmatory instrument or assignment forwarded to the contracting officer? No

Foreign Countries of application:

Papers: You must enter/upload all Publications, Conference Proceedings, Books, Dissertations, Thesis and Manuscripts for the reporting period.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Paper published in peer-reviewed journal (N/A for none)
Number of papers published in peer –reviewed journals: 11

List of papers

1. D. J. Crain, J. E. Garland, S. E. Rock and D. Roy "Quantitative characterization of silicon solar cells in the electro-analytical approach: Combined measurements of temperature and voltage dependent electrical parameters", Anal. Methods 4 (2012) 106-117.
2. D. J. Crain, J.P. Zheng, C.M. Sulyma, C. Goia, D.Goia, D. Roy, "Electrochemical features of ball-milled lithium manganate spinel for rapid-charge cathodes of lithium ion batteries", J. Solid State Electrochem. (2012) DOI 10.1007/s10008-012-1677-8.
3. C. M. Sulyma, C. M. Pettit, J. E. Garland, D. Roy, "Surface plasmon resonance as a probe of interactions between a thin-film gold electrode and an aqueous supporting electrolyte containing 1-ethyl-3-methyl-imidazolium ethyl sulfate ionic liquid", Surf. Interface Anal. (2012), DOI: 10.1002/sia.4808.

4. L. Wu, J. Jasinski, S. Krishnan, “Carboxybetaine, Sulfobetaine, and Cationic Block Copolymer Coatings: A Comparison of the Surface Properties and Antifouling Behavior,” J. Appl. Polym. Sci. 124 (2012), 2154-2170.
5. J.E. Garland, D.J. Crain and D. Roy, “Impedance spectroscopy coupled with voltammetry for quantitative evaluation of temperature and voltage dependent parameters of a silicon solar cell”, Solar Energy 85 (2011) 2912-2923.
6. J.E. Garland, D.J. Crain, J.P. Zheng, C.M. Sulyma and D. Roy, “Electro-analytical Characterization of Photovoltaic Cells by Combining Voltammetry and Impedance Spectroscopy: Voltage Dependent Parameters of a Silicon Solar Cell under Controlled Illumination and Temperature”, Energy Env. Sci. 4 (2011) 485-498.
7. L. V. N. R. Ganapatibhotla, L. Wu, J. P Zheng, X. Jia, D. Roy, J. B. McLaughlin and S. Krishnan, “Ionic liquids with fluorinated block-oligomer tails: Influence of self-assembly on transport properties”, J. Mater. Chem. 21 (2011) 19275-19285.
8. J.P. Zheng, D.J. Crain and D. Roy, “Kinetic aspects of Li intercalation in mechano-chemically processed cathode materials for lithium ion batteries: Electrochemical characterization of ball-milled $LiMn_2O_4$”, Solid State Ionics 196 (2011) 48-58.
9. E. Martinelli, G. Galli, S. Krishnan, M .Y. Paik, C. K. Ober, D. A. Fischer, “New poly(dimethylsiloxane)/poly(perfluorooctylethyl acrylate) block copolymers: structure and order across multiple length scales in thin films”, J. Mater. Chem. 21 (2011), 15357-15368.
10. L. V. N. R. Ganapatibhotla, J. Zheng, D. Roy, S. Krishnan, “PEGylated imidazolium ionic liquid electrolytes: thermophysical and electrochemical properties”, Chem. Mater. 22 (2010), 6347-6360.
11. S. Krishnan, M. Y. Paik, C. K. Ober, E. Martinelli, G. Galli, K. E. Sohn, E. J. Kramer, and D. A. Fischer, “NEXAFS depth profiling of surface segregation in block copolymer thin films,” Macromolecules, 43 (2010), 4733-4743.

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)
Number of papers published in non peer-reviewed journals: 0
List of papers: N/A

(c) Papers presented at meetings, but not published in conference proceedings:
Number of Papers presented but not Published: 4
List of papers:

1. S. Krishnan, J. L. Lebga, L. Wu, J. B. McLaughlin, S. Rock, D. Roy, “Thermophysical and Electrochemical Properties of Self-Assembling Amphiphilic Ionic Liquids,” Talk presented at the 2012 AIChE Annual Meeting, October 28-November 2, 2012, Pittsburgh, PA.
2. J. B. McLaughlin, S. Krishnan, L. Wu, L. V. N. R. Ganapatibhotla, X. Jia, D. Roy and J.P. Zheng, “Self-Consistent Field Modeling of Microstructure Formation in Fluorinated "Block" Ionic Liquids for Photovoltaic Cells”, Talk presented at the 2011 AIChE Annual Meeting, October 16-21, 2011, Minneapolis, MN.
3. L. Ganapatibhotla, J. P. Zheng, D. Roy and S. Krishnan, "Solid Organic Electrolytes and Ionic Liquids, with Poly(ethylene glycol) and Semifluorinated Alkyl Side Chains, for Photovoltaic and Energy Storage Applications", Presented at the 2010 AIChE Annual Meeting, Salt Lake City, Utah, November 7-12, 2010.
4. D. Roy, “Electro-Analytical Characterization of Solar Cells”, Talk presented at the Center for Advanced Materials Processing Fall 2010 Symposium, Potsdam, NY; October 14, 2010.

(d) Non Peer-Reviewed Conference Proceeding publications (other than abstracts):
Number of Non Peer-Review Conference Proceeding publications (other than abstracts): 7
List:

1. L. Wu, S. Rock, D. Roy, J. B. McLaughlin, and S. Krishnan, “Structure–Property Correlations in Block-Oligomer Ionic Liquid Electrolytes,” The 2012 Annual Meeting of the Center for Advanced Materials Processing, Albany, New York (May 2012).

2. D. J. Crain, J. P. Zheng and D. Roy, "Characterization of Rapid-Recharge Li ion Batteries", Poster presented at the CAMP Fall Meeting, October 10-11, 2011.
3. D. J. Crain, J.P. Zheng D. Roy, "Characterization of Electrode Materials for Li ion Batteries with Improved Cyclability", Poster presented at the Annual Technical Meeting of CAMP; May 19, 2011.
4. L. Wu, S. Krishnan, X. Shi, D. Roy, "Electrochemical Properties of Novel PEGylated Electrolyte Blend for Dye Sensitized Solar Cells and Lithium Ion Batteries", Poster presented at the Annual Technical Meeting of CAMP; May 19, 2011.
5. J. E. Garland, D. J. Crain, S. E. Rock, D. Roy, "Electroanalytical Characterization of Resistive Power Losses in a Single Crystal Silicon Solar Cell", Poster presented at the Annual Technical Meeting of CAMP; May 19, 2011.
6. D.J. Crain, J. P. Zheng and D. Roy, "Characterization of Electrode Materials for Rapid-Recharge Li ion Batteries", Poster presented at the Center for Advanced Materials Processing Fall 2010 Symposium, Potsdam, NY; October 14, 2010.
7. S. Krishnan**,** "Nanostructured Electrolytes with Low Fluidity and High Conductivity for Solar Cells and Fuel Cell Membranes", Clarkson University Center for Advanced Materials Processing, 2011 Annual Technical Meeting (May 20, 2011).

(e) Manuscripts:
Number of Manuscripts: 1
List:

1. S. E. Rock, L. Wu, D. J. Crain, S. Krishnan, and D. Roy "Interfacial Electrochemistry of a Solvent Free PEGylated Imidazolium Bistriflamide Ionic Liquid Electrolyte at a $LiMn_2O_4$ Cathode for Lithium Ion Batteries," manuscript for ACS Appl. Mater. Interfaces.

(f) Books
Number of Books: 0
List:
N/A

Honors and Awards:

A report of our project has been featured in the special themed issue on "Future Electroanalytical Developments" of the journal [Crain et al., Anal. Methods 4 (2012) 106 – 117, published by RSC]"

Patents:

Number of Patents Submitted: 1
List of Patents Submitted:
Solid Organic Electrolytes, U. S. Patent Application no. 12/778,410 (2010).

Number of Patents Awarded: 0
List of Patents Awarded: N/A

Graduate Students: Percent support is percent (0 -1) of total time person was supported by this grant for the reporting period.

Name	Percent Supported	Discipline of Degree
John Garland	17.4% of 2010-11 stipend	Physics PhD
Daniel Crain	0%	Physics PhD
Jianping Zheng	0%	Physics PhD
Lalitha Ganapatibhotla	0 %	Chemical Engineering MS

Lin Wu	100 % of 2010-11 stipend	Chemical Engineering PhD

Post Doctorates: Percent support is percent (0 -1) of total time person was supported by this grant for the reporting period. 0

Name	Percent Supported
Xinli Jia	40 %

17) Undergraduate Students

Name	Percent Supported	Discipline of Degree
Tyler Mosher	0%	Physics B.S.
Theodore Glave	0 %	Chemical & Biomolecular Engineering B.S.
Sydney Laramie	0 %	Chemical & Biomolecular Engineering B.S.
Joshua Franclemont	0 %	Chemical & Biomolecular Engineering B.S.

Student Metrics:

All items refer to graduating undergraduates funded by this agreement and the reporting period for this report.

1. Number of graduating undergraduate students: 2 (Theodore Glave, May 2011, and Joshua Franclemont, May 2012)

2. Number of undergraduate students graduating with degrees in science, mathematics, engineering, and technology fields: 2

3. Number of graduating undergraduates who will continue to pursue graduate degrees: 2

4. Number of graduating undergraduates who intend to work for the Defense Department: Unknown

5. Number of graduating undergraduates during this period who achieve a 3.5 to 4.0 GPA (Convert GPAs on any other scale to be an equivalent value on a 4.0 scale.): 2

6. Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: 0

7. The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 2

Masters Degree Awarded: Percent support is percent (0 -1) of total time person was supported by this grant for the reporting period.

Name: Lalitha Ganapatibhotla **Percent Supported: 0**

Doctorate Degrees Awarded: Percent support is percent (0 -1) of total time person was supported by this grant for the reporting period.

Name	**Percent Supported**
John Garland	17.4% of 2010-11 stipend
Daniel Crain	0%
Jianping Zheng	0%

Faculty: Percent support is percent of total time person was supported by this grant for the reporting period.

Name	**Percent Supported**	**National Academy Member**
Sitaraman Krishnan	4.16 %	N/A
Dipankar Roy	0%	N/A
John McLaughlin	0 %	N/A

Other Staff: Percent support is percent (0 -1) of total time person was supported by this grant for the reporting period.
Postdoctoral Research Associate

Name	**Percent Supported**
Xinli Jia	40 % (2011)

Scientific Progress and Accomplishments: Scientific progress and accomplishments (Description should include significant theoretical or experimental advances) Plain Text Only - If you have diagrams, formula's, etc. in a Word, PDF or other document, enter "See Attachment" below and use the "Attachment" section at the bottom of the menu. This section can include, but is not limited to: (1) Foreword (optional) (2) Table of Contents (if report is more than 10 pages) (3) List of Appendixes, Illustrations and Tables (if applicable) (4) Statement of the problem studied (5) Summary of the most important results (6) Bibliography (7) Appendixes.

Project 2:

Problems studied

Since most commonly used organic liquid electrolytes of dye sensitized solar cells (DSSCs) are volatile and flammable, they limit the long-term stability and high temperature operations of these cells. We have addressed these issues through the development and characterization of non-volatile, non-flammable and polymerizable IL electrolytes. In a parallel effort, we have developed an electro-analytical approach to quantitative testing of laboratory scale photovoltaic cells. Since the IL electrolytes should also be usable for certain energy-storage as well as sensor devices, we have investigated supporting active materials for energy storage, focusing specifically on $LiMn_2O_4$ cathodes for Li ion (solar) batteries. Furthermore, we have explored the adsorption characteristics of ILs on Au thin films for sensor-type applications.

Summary of the most important results

We have synthesized and characterized an imidazolium iodide ionic liquid containing an ω-perfluoroalkyl poly(ethylene glycol) (PEG) tail [1]. The solid phase of this material was accomplished through the generation of ionic clusters by electrostatic interactions, as well as through microphase separation of the immiscible perfluoroalkyl and PEG segments of the cation used. We have performed self-consistent mean field calculations to probe the formation of nanostructures in the ionogel. The high conductivity, and the non-volatile, gel-like properties of this electrolyte will be useful to support the function of high-performance, leakage-proof DSSCs. We have also synthesized and characterized certain PEGylated ILs [2]. These latter ILs exhibit satisfactory conductivities (~0.13 mS cm^{-1}at room temperature) despite their relatively high viscosities, and support a temperature-independent electrochemical window of ~2 V.

We have developed an electro-analytical approach to quantitative characterization of solar cells. Crystalline Si cells have been used to establish the analytical protocols of this method [3-6]. We have demonstrated how this method can evaluate the temperature and voltage sensitive features of the minority carrier lifetimes, series and shunt resistances and back surface field parameters of a solar cell. Apart from displaying their characteristic temperature dependencies, the parameters measured in this way have responded to variations of the cell voltage, and exhibited mutually interacting features of the observed effects [3-5]. These results have shown how the characteristic features of charge recombination in the quasi-neutral and space charge regions of the solar cell could be resolved with D.C. voltage dependent A.C. impedance measurements.

The diode-like electrical behavior of a DSSC has been studied to evaluate the detailed charge recombination characteristics of the cell [6]. A forward biased dark DSSC has been used to preferentially activate the recombination reactions, and the kinetics of these reactions have been probed by using electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). The ohmic and non-ohmic series resistances of the DSSC have been separated, and their origins have been investigated. The characteristic impedance parameters of the different active interfaces of the multi-component solar cell have been obtained from complex nonlinear least square (CNLS) analysis of the EIS data. Among these parameters, the electron lifetime and the resistance of charge transfer at the TiO_2-electrolyte interface have followed the same diode-like voltage dependence of the D.C. current. We have shown that, this diode feature of the DSSC played a critical role in determining the overall performance of the cell.

The electro-analytical studies of DSSCs carried out through our project show that, strategically selected experimental control variables, coupled with CNLS analysis of experimental data can enable the component-specific resolution of EIS.

This in turn helps to resolve the individual impedance parameters of the FTO-TiO_2 and Pt-FTO interfaces from those of the TiO_2 anode film in a DSSC [6]. EIS also detects the different electrical characteristics of the morphologically different TiO_2 layers included in the photo-anode of the cell. Furthermore, the power-consuming series resistance (R_s) of the DSSC is determined directly from CNLS-analyzed EIS results; the ohmic and non-ohmic components of this resistance also are resolved in this approach [6]. These R_s data facilitate an accurate evaluation of the internal voltage of the DSSC, and allow for a rigorous examination of the cell's electrical attributes.

We have tested a cathode of lithium manganese oxide using a mixture of nanometric and micrometric active particles [7,8]. The goal of this specific study was to explore selected materials for energy storage components (such as Li ion solar batteries) that could be integrated with solar powered devices. To conduct these experiments, commercially available particles were mechano-chemically modified by ball-milling. Ragone plots, recorded using galvanostatic measurements indicated enhanced power delivery characteristics of the ball-milled material compared to its unprocessed counterpart [8]. The processed material also exhibits improved resistance against electrolyte reactions and surface film formation. Due to these advantageous electrochemical attributes, the ball-milled cathode material also has served as an adequately suited system for exploring various fundamental aspects of Li intercalation [8]. Scan rate dependent slow scan cyclic voltammetry has helped to identify the kinetic and diffusion controlled features of Li transport in the processed active particles. The observations have been substantiated further by using EIS and by measuring the voltage dependent charge transfer resistance and diffusion coefficient of Li transport.

We have combined SPR and electrochemical measurements to study the interactions of a gold film electrode with concentration dependent electrolytes of an IL [9]. The purpose of this particular study was to understand the adsorption characteristics of an IL on a typical sensing electrode, and to further explore IL based device applications. Voltage- and/or electrolyte-induced variations were detected in the critical angles and SPR angles measured in the attenuated total reflection geometry. The optical response of the bulk electrolyte strongly affected the SPR angles; the critical angle data helped to separate these effects from those arising strictly from the electrode surface. The optical parameters of the Au-electrolyte system were determined by fitting the SPR angle-spectra to calculated results of a multi-layer reflectivity model. The results demonstrated how angle resolved SPR measurements could be used to determine the surface adsorption characteristics of ILs.

Bibliography

1. L. V. N. R. Ganapatibhotla, L. Wu, J. P Zheng, X. Jia, D. Roy, J. B. McLaughlin and S. Krishnan, "Ionic liquids with fluorinated block-oligomer tails: Influence of self-assembly on transport properties", J. Mater. Chem. 21 (2011) 19275-19285.
2. L. V. N. R. Ganapatibhotla, J.P. Zheng, D. Roy and S. Krishnan, "PEGylated Imidazolium Ionic Liquid Electrolytes: Thermophysical and Electrochemical Properties", Chem. Mater. 22 (2010) 6347–6360.
3. D. J. Crain, J. E. Garland, S. E. Rock and D. Roy "Quantitative characterization of silicon solar cells in the electro-analytical approach: Combined measurements of temperature and voltage dependent electrical parameters", Analytical Methods 4 (2012) 106-117.
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5. J.E. Garland, D.J. Crain, J.P. Zheng, C.M. Sulyma and D. Roy, "Electro-analytical Characterization of Photovoltaic Cells by Combining Voltammetry and Impedance Spectroscopy: Voltage Dependent Parameters of a Silicon Solar Cell under Controlled Illumination and Temperature", Energy Env. Sci. 4 (2011) 485-498.
6. J.E. Garland, Ph.D. Thesis, Clarkson University (2011).
7. D. J. Crain, J.P. Zheng, C.M. Sulyma, C. Goia, D.Goia, D. Roy, Electrochemical features of ball-milled lithium manganate spinel for rapid-charge cathodes of lithium ion batteries, J. Solid State Electrochem. 16 (2012) 2605-2615.

8. J.P. Zheng, D.J. Crain and D. Roy, "Kinetic aspects of Li intercalation in mechano-chemically processed cathode materials for lithium ion batteries: Electrochemical characterization of ball-milled $LiMn_2O_4$", Solid State Ionics 196 (2011) 48-58.
9. C. M. Sulyma, C. M. Pettit, J. E. Garland, D. Roy, “Surface plasmon resonance as a probe of interactions between a thin-film gold electrode and an aqueous supporting electrolyte containing 1-ethyl-3-methyl-imidazolium ethyl sulfate ionic liquid”, Surf. Interface Anal. 44 (2012) 801-810..

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3. List of Appendixes, Illustrations and Tables (if applicable)
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5. Summary of the most important results
6. Bibliography
7. Appendixes

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